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Comparison of techniques for the measurement of carbon dioxide evolution from soil

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With 3 figures

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1. Introduction

For research in the fields of soil science, plant physiology, and soil microbiology, it is of interest to know how much organic matter is broken down in the soil annually.

The simplest approach to the decomposition rate is measurement in the field of released carbon dioxide as a measurable end product of all the conversions leading to the total mineralization of these carbon compounds. The long series of publications on this subject (see Haber 1958, Reiners 1968, Macfadyen 1970) reveal the wide divergance of the results obtained by various authors. A ratio of 1 : 20 in the measured quantities is not unusual (Macfadyen 1970). To the best of our knowledge, a critical comparative study of the techniques used in this work had not yet been performed. The present investigation represents a contribution toward the elimination of this hiatus.

2. Past research

The published techniques can be divided into four types: open vessels (I) or domes with the open end placed on the ground and closed vessels (II). Open vessels are used in three variants. (Ia) In the dome an equilibrium is reached between the gases originally in the dome and those in the soil. Gas samples are taken periodically and analysed to determine the carbon dioxide content. The volume of gas removed is replaced by air lacking carbon dioxide. This method was used by Lundegårdh (1924) and Fehér (1933). (Ib) The dome contains an absorbent for carbon dioxide (alkali or soda lime). After a given period, the amount of CO_2 in the absorption medium is determined. Lundegårdh (1924), Haber (1958), Froment et al. (1969), Monteith et al. (1964). (Ic) At one side of the dome air is introduced, sometimes CO_2-free, and at the other side the air passing over the soil and containing the CO_2 it has taken up in the process, is led through an absorption agent or through an infrared spectrophotometer. Porkka (1931), Witkamp (1966, 1969), Witkamp and Frank (1969), Reiners (1968).

In using closed vessels (II) a soil sample is placed in a sealable jar, and the released CO_2 is absorbed, as was done by Isermeyer (1952), or determined with an infrared spectrophotometer, as done by Koepf (1953). The results obtained with all these techniques (under paragraphs 2) mainly concern observations made in widely differing places and in different months of the year. As a rule, the measurement periods were rather short; only a few authors maintained their measurements for several months to a year. A recent review has been given by Macfadyen (1970).

Porkka criticized techniques of the first type (Ia) as early as 1931, mainly on the basis of the phenomenon that under the dome there is an accumulation of CO_2 that would influence the diffusion rate of the CO_2 from the soil.

3. The present study

3.0. General remarks

On the basis of the foregoing, we performed a comparative study to determine the extent to which the various techniques give the same results and the degree to which the principle of carbon dioxide measurement in the field serves a useful purpose.

The determination of the quantity of carbon dioxide diffusing from the soil into open vessels means that the volume of soil from which the carbon dioxide originates is not known. To avoid this uncertainty, carbon dioxide evolution should preferably be measured in isolated soil columns that have been previously exposed for an adequate period to all the normal climatological conditions before isolation. For this purpose, we have at our disposal 11-year-old lysimeters which can be completely sealed off from the atmosphere. The evaluated techniques belong to the types mentioned above.

3.1. Equipment used and experimental set-up

Plastic pails holding 5 or 20 litres with an opening measuring 3 and 6.5 dm^2, respectively, were placed with the opening against the ground, and some soil was packed over the curved rim. Each spot to be provided with one of these pails was provided in advance with a jar containing alkali or a petri dish containing soda lime, both raised a few centimetres above the surface of the soil.

Glass vessels (1 litre) which could be closed with a glass lid and a rubber ring (preserving jars) were provided with a soil sample. The soil sample was either placed within a plastic or metal ring or was simply allowed to fall into the jar. The absorption agent was placed a few cm above the upper surface of the soil sample.

Lysimeters, i. e. preservative-treated wooden tanks with a content of 230 litres and an effective surface of 27 dm^2, filled in 1958 with forest soil lying undisturbed on a bed of sand. These containers have a foot standing in a concrete tub which can be filled with 15 cm water. During experiments, the tank is surrounded with a zinc jacket whose upper rim is provided with a gutter which can be filled with water and serves as a water seal for a Perspex cap used to close the container. The cap is provided with openings for the attachment of tubes.

For the experimental set-up in which a current of air carries off the released CO_2, CO_2-free air is introduced into the lysimeter via a manifold of tubing permitting even distribution over the soil in the container. The removal of air that has taken up CO_2 is effected by a single outlet via a series of gas-washing bottles and a suction pump. The absorbed CO_2 is determined periodically by titration of the alkali. The rate of the air flow amounts to 22 litres per hour. The "dead" space between the ground and the cap is about 132 litres.

For an experimental set-up in which alkali kept in motion absorbs the CO_2 emerging from the soil, a similar lysimeter tank is used. A peristaltic pump in the tank serves to draw the alkali up from and flush it back into a jar. This agitates the alkali and prevents the formation of a carbonate scum. The agitation also provides optimal conditions for absorption.

For an experimental set-up with a stationary absorption agent and without ventilation, the lysimeter with cap may be regarded as a large closed vessel with a stabilized soil sample.

4. Results

4.1. Open vessels

4.1.1. The influence of the exposure time on the absorbed CO_2 flux

Site, etc.: Garden soil in situ, bare surface without vegetation. Soil area covered by the pails: 6.5 dm^2; content 10 litres. Absorption medium: 60 ml KOH solution 0.3 N. Temperature — diurnal: 27 °C, nocturnal: 10.5 °C; daily mean: 16.5 °C. Time: June 1970. Mean CO_2 absorption over a period of 0—3 hours (0.34 mg/dm^2/hour) and 0—3 hours to 24 hours (1.08 mg ($\pm$0.07)/dm^2/hour). The absorption curve is shown in Fig. 1. These results make it likley that the total absorption increases linearly and proportionally with time. The slope of the curve shows a mean increase of 1.2 mg CO_2/dm^2/hour, which is in good agreement with the mean calculated for exposure times of more than 3 hours. The reason why highly divergent values are found for short exposure times remains obscure.

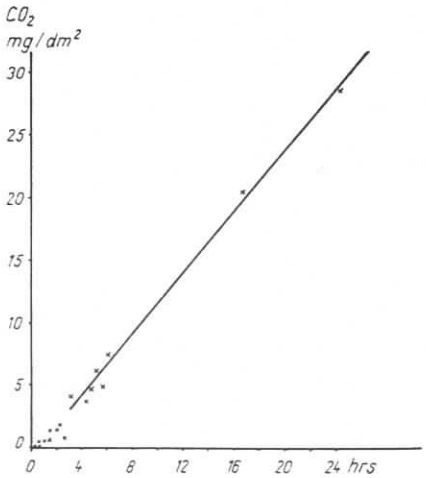

Fig. 1 Quantities of carbon dioxide evolved from soil in relation to the duration of exposure to the absorbing agent.

4.1.2. The influence of concentration of the absorption medium on the absorbed CO_2 flux

Site, etc.: Garden soil in situ, bare surface without vegetation. Soil area covered by the pails: 3 dm²; content 5 litres. Absorption media: 5 g soda lime, 60 ml KOH in a graduated series of concentrations.

In all cases care was taken that at the end of each exposure period a sufficient reserve of unused alkali was present. At the lowest titre, 85 % of the available alkali was used, in all the other cases much less than 50 %.

The results pertaining to the various alkali concentrations are shown in Fig. 2. There is a certain correlation between the amount of CO_2 absorbed per time unit and the logarithm of the titre, but this becomes uncertain at higher titres. Above 0.25 N. the quan-

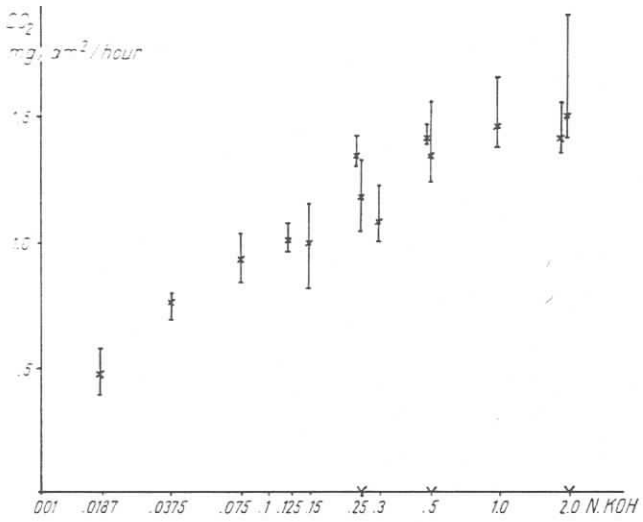

Fig. 2 Carbon dioxide flux in relation to the titre of the absorbing alkali.

tity of CO_2 absorbed per time unit shows little or no increase at increasing titre. Haber (1958) also found almost no detectable difference in CO_2 absorption between 0.5 and 2 N alkali. It would be wrong however to conclude that all the CO_2 formed is absorbed by the alkali in higher concentrations, because the amounts of CO_2 absorbed by soda lime lie appreciably higher than those for alkali, i. e. 2.13 ($\pm$ 0.078) mg/dm²/hour. It is not impossible that the relative increase of the inert carbonate concentration in the solution impedes the diffusion of CO_2. The size of the surface area covered by these domes has no influence on the CO_2 absorption; this is evident from a comparison of the values of 1.08 $\pm$ 0.04 and 1.08 $\pm$ 0.07 mg/dm²/hour found for the small (3 dm²) and the large (6.5 dm²) pails respectively.

4.2. Closed vessels

Carbon dioxide evolution from soil samples. From garden soil in situ, soil samples were taken with metal rings (area 0.4 dm², content 106 cm³). The samples were assigned to one of three groups: samples placed in the measuring container still in the ring; samples removed from the ring, mixed, and returned to the ring for placement in the measuring container; samples removed from the ring and allowed to fall into the measuring container.

The absorption medium was placed a few centimetres above the soil sample. Absorption media: 5 g soda lime or 60 ml KOH solution of 0.5 or 2.0 N. Measuring was done 16 hours later (overnight period). During this period, the measuring containers were kept in the soil in the garden. The content of these containers (preserving jars) was 1 litre. The results are shown in Table 1.

Table 1 Carbon dioxide evolution from soil samples in closed vessels

Absorption media	Absorbed CO_2 (mg/dm²/hr)		
	Undisturbed sample	Disturbed sample	
		in ring	loose
KOH 2.0 N	1.6 $\pm$ 0.13 (n = 4)	–	1.35 $\pm$ 0.12 (n = 3)
0.5 N	1.22 $\pm$ 0.12 (n = 7)	1.6 $\pm$ 0.10 (n = 7)	–
Soda lime	3.38 $\pm$ 0.09 (n = 6)	3.6 $\pm$ 0.16 (n = 3)	2.6 (n = 1)

The differences between undisturbed and disturbed samples and between the alkali concentrations are clearly not significant or only barely significant. The difference between alkali and soda lime is significant. No significant differences can be demonstrated between the values obtained in these experiments and those obtained in the open vessels described above, with respect to the absorption by alkali, but the opposite is the case for the values obtained with soda lime, i. e. 2.13 $\pm$ 0.08 mg/dm²/hour (n = 10) and 3.38 $\pm$ 0.09 mg/dm²/hour (n = 10).

4.3. Lysimeter tanks without plants

4.3.0. General remarks

In our opinion, the soil in these tanks may be considered as soil in the natural situation and as being under virtually the same conditions as soil in situ. The soil in the tanks used in this study contains slightly less organic matter than the garden soil mentioned above. The advantage offered by the lysimeter tanks is that the volume of the soil from which the CO_2 evolves is known. The possibility of any lateral diffusions is excluded.

4.3.1. Absorption by 10—25 g soda lime (grain size: 1.5—2.5 mm)

Time: September—October 1970. The results are shown in Table 2.

From the total amount of absorbed CO_2, the amount of CO_2 normally present in the air of the dead space under the cap is subtracted before calculation of the absorption per hour from the remainder. The nocturnal absorption is extremely steady, amounting to 0.995 ± 0.03 mg/dm²/hour. The diurnal absorption is highly variable, 1.0 ± 0.26 mg/dm²/hour, as found so far with all the absorption medium used.

Table 2 Carbon dioxide evolution in lysimeter tanks

	Observation period (hr)	Absorbed CO_2 mg/dm²/hr)	Mean soil temp. (°C)
29/IX—30/X 1971	21.7	0.99	16
30/IX—1/X	22.9	0.99	15
1/X	3.2	1.67	16
1—2/X	19.2	1.10	14
2/X	2.2	0.70	17
2—5/X	69.0	0.78	13
5/X	1.9	0.42	15
5—6/X	20.2	1.04	14
6/X	3.6	0.70	16
7/X	2.9	1.58	16
7—8/X	18.8	0.97	14
8—9/X	18.6	0.88	13

For the nocturnal data obtained in this material, no significant correlation has been found between the amount of absorbed CO_2 and temperature and/or air pressure.

4.3.2. Absorption by various quantities of soda lime (grain size: 2—6 mm)

In Fig. 3 the amount of soda lime used is plotted against the corresponding values of absorbed CO_2 per hour. These data pertain to periods averaging 18 hours, including the nocturnal hours. As in 4.3.1. shorter observation periods during the day showed a high degree of variability and led to no conclusions.

The graphical data indicate a strong correlation between the amount of soda lime used and the amount of CO_2 absorbed per hour ($r = +0.89$).

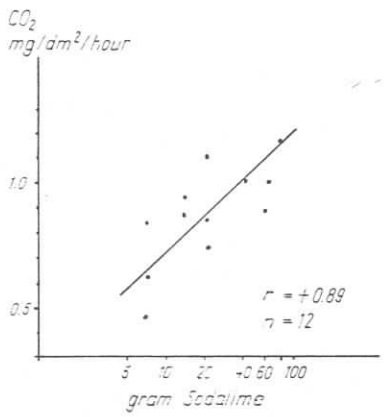

Fig. 3 Carbon dioxide flux in relation to the quantities of soda lime used as an absorbing agent.

Although the data under a and b were not obtained under exactly the same conditions, analysis shows significant differences in the amount of absorption due to differences in the grain size of the soda lime: at a grain size of 1.5 to 2 mm, absorption is greater than at a grain size of 2 to 5 mm.

4.3.3. Absorption by an alkali solution kept in motion by a small pump

The experimental periods of 15 or more hours show wide differences in the mean absorption between 60—240 m*l* 0.3 N and 180 m*l* 0.9 N KOH. The results are 0.49 ± 0.04 and 1.32 ± 0.09 mg CO_2/dm^2/hour with $n = 11$ and $n = 8$, respectively, and the soil temperatures 20 °C and 15 °C, respectively. All observations were done in the same tank. Except for the titre of the alkali solution, all conditions were virtually identical.

4.3.4. Absorption by flowing air

Before the measurements were started, the air flow was maintained for at least 24 hours.

For an assumed carbon dioxide evolution of 1 mg/dm²/hour, it was calculated that after 24 hours the carbon dioxide supple from the soil and the amount of carbon dioxide removed from the tank were in quilibrium at the pump capacity applied. No significant differences in the amount of absorbed carbon dioxide were found for alkali concentrations of 0.3 and 2.0 N in the gas washing bottles.

The measured mean carbon dioxide fixation amounted to 0.90 ± 0.08 mg/dm²/hour ($n = 20$). This value differs significantly from the value of 1.32 ± 0.09 mg/dm²/hour mentioned under 4.3.3.

4.4. Lysimeter tank with grass and herbaceous plants

4.4.1. Absorption by alkali solution kept in motion

In this case the amount of nocturnally absorbed CO_2 lies significantly higher than the diurnal values, i. e. 2.67 ± 0.12 mg dm²/hour ($n = 19$) as against 1.27 ± 0.10 ($n = 19$). The influence of the photosynthesis occurring during the day is very clear here. This series showed a significant correlation between the amount of CO_2 absorbed per hour and the soil temperature, but this correlation was not found in any of the other series.

4.4.2. Absorption by stationary alkali

Absorbent: 250 m*l* KOH solution 2.6 N. Here too, there is a significant difference between the diurnal and nocturnal values i. e. 0.64 ± 0.10 and 1.22 ± 0.08 mg/dm²/hour, respectively.

5. Discussion

During two different seasons and in different ways, a particular type of soil was submitted under different conditions to relatively long series of analyses of the evolution rate of carbon dioxide. Of the data collected, only those which were mutually comparable were used. These results are shown in Table 3.

On the basis of the present results, the most recommendable method is absorption by fine-grained soda lime. This absorbent gives the highest values, and there is no reason to assume that under its influence more carbon dioxide is evolved or more might enter under the rim of the vessel than would be the case for 2 N alkali.

Table 3 Carbon dioxide evolution from garden soil under various conditions(in mg/dm²/hr)

Experimental set-up	Duration (hr)	Absorption media KOH solution (in titres)						Soda lima		
		stationary				agitated		flowing air	fine	coarse
		0.3	0.5	0.9	2.0	0.3	0.9			
a. soil without growing plants										
1. closed vessels										
undisturbed samples	24	—	1.22	—	1.6	—	—	—	3.38	—
disturbed samples	24	—	1.35	—	1.6	—	—	—	3.10	—
2. open vessels										
3 dm²	18	1.08	—	—	—	—	—	—	2.13	—
6.5 dm²	18	1.08	—	—	—	—	—	—	—	—
3. lysimeter tank	18	—	—	—	—	0.49	1.32	0.90	0.99	0.84
b. soil with growing plants lysimeter tank										
nocturnal	16	—	—	—	1.22	—	—	2.67	—	—
diurnal	4	—	—	—	0.64	—	—	1.27	—	—

What must be taken into consideration, however, is the fact that the amount of soda lime applied has an influence on the level reached by absorbed carbon dioxide, i. e. the absolute value with respect to carbon dioxide evolution from the soil is disputable.

The data obtained with a lysimeter tank show a good agreement between the results obtained with the pump technique and those obtained with soda lime (see Table 3), the latter being much simpler to perform. On the basis of the data obtained with the vegetated tank, the use of stationary alkali is certainly not advisable.

It seems to us that the above-described techniques are only suitable for the comparison of different objects, since only an approximation of the true amount of released carbon dioxide can be obtained. A good example of this is also found in the studies done by REINERS (1968) and WITKAMP and FRANK (1969), in which highly divergent results were obtained i. e. 2912 g/m² as against 1130 g/m²/year. Both with an almost identical technique of I. R. absorption and an annual litterfall which was roughly the same in the two forests under study.

The usefulness of isolated samples in closed vessels cannot be determined from our results, because only one sample size was applied and only a 24-hour observation period was taken; under these conditions the carbon dioxide evolution was one and a half times higher than was observed for the same soil during field observations (i. e. 1.2 and 1.08 mg/dm²/hour for 4.1.1. and 4.1.2. respectively).

It proved to be impossible to determine a Q10 value from our observations. Only one series of nocturnal observations in a tank with growing plants showed a correlation between soil temperature and carbon dioxide evolution. For the determination of a Q10 value it is necessary to have more control over the environment than could be reached under our conditions. In the field the level of carbon dioxide evolution is not determined solely by temperature. A correlation with changes in air pressure could not be demonstrated. Another possible factor as a result of which field observations give higher values than measurements in a tank without growing plants, is the root respiration of trees in the vicinity This problem of root respiration adds to the questionable aspect of the measurement of carbon dioxide evolution for carbon balance studies.

6. Summary · Zusammenfassung

A critical investigation of techniques for the determination of carbon dioxide evolution from the soil is reported. Use was made of open and closed vessels provided with soda lime and alkali as absorption agents, and with and without flowing air cas carbon dioxide carrier. For general comparative studies, various techniques are found to be suitable if large observation periods are applied (more than 15 hours). For the determination of the absolute carbon dioxide evolution, only an approximation can be reached. It is thus doubtful whether this determination has any value at all for a carbon dioxide balance analysis or for a description of the biological activity in the soil, since in the field root respiration cannot be excluded from the measurements. A Q10 determination for soil in situ proved not to be feasible, because other factors besides temperature and air pressure probably play a rôle in carbon dioxide evolution.

[Vergleich von Techniken zur Messung der Kohlendioxid-Freisetzung aus dem Boden]

Die Zuverlässigkeit von Techniken zur Messung der Kohlensäurefreisetzung aus Freilandboden wurde geprüft. Dazu wurden offene bzw. geschlossene Gefäße mit und ohne Luftdurchfluß verwendet; als Absorbientien dienten Natronkalk und Kalilauge in verschiedenen Konzentrationen.

Es stellte sich heraus, daß für ungefähre und vergleichende Messungen mehrere Techniken anwendbar sind, aber nur mit ziemlich langer Beobachtungszeit (> 15 h). Für die Bestimmung des Absolutwertes der Kohlensäurefreisetzung, wie man ihn für die Erstellung einer Kohlenstoffbilanz benötigt, ist nur ein Annäherungswert zu erzielen. Es ist zweifelhaft, ob dieser Wert eine Basis für eine totale C-Bilanz oder für die Schätzung der biotischen Aktivität im Boden bieten kann, denn im Freiland kann die Wurzelatmung nicht eliminiert werden.

Eine Q_{10}-Bewertung des intakten Bodens war nicht zu erzielen, weil neben der Temperatur und dem Luftdruck auch andere Faktoren die Freisetzung der Kohlensäure beeinflussen.

7. Bibliography

Fehér, D., 1933. Untersuchungen über die Mikrobiologie des Waldbodens. Berlin, Julius Springer. IV + 272 pp.

Froment, A., and F. Mommaerts-Billiet, 1969. La respiration du sol, l'azote minéral et la décomposition des feuilles de chêne et de hêtre en relation avec les facteurs de l'environnement. Bull. Soc. Roy. Botan. Belgique. **102**, 387–410.

Haber, W., 1958. Ökologische Untersuchung der Bodenatmung. Flora **146**, 109–157.

Isermeyer, H. 1952. Eine einfache Methode zur Bestimmung der Bodenatmung und der Karbonate im Boden. Z. Pflanzenernähr. Düng. Bodenkunde **56**, 26–38.

Koepf, H., 1953. Die Temperatur/Zeit-Abhängigkeit der Bodenatmung. Z. Pflanzenernähr. Düng. Bodenkunde **61**, 29–48.

Lundegårdh, H., 1924. Der Kreislauf der Kohlensäure in der Natur. Jena, Gustav Fischer. 308 pp.

Macfadyen, A., 1970. Soil metabolism in relation to ecosystem energy flow and to primary and secondary production. In: Phillipson, J. (ed.): Methods of study in soil ecology. Proceedings of the Paris Symposium. Unesco – I. B. P. 1967. 167–172.

Monteith, J. L., G. Sceicz and K. Yabuky, 1964. Crop photosynthesis and the flux of carbon dioxide below the canopy. J. appl. Ecology **1**, 321–337.

Porkka, O. H., 1931. Über eine neue Methode zur Bestimmung der Bodenatmung. Ann. Soc. Zool.-Bot. Fenn. **15**, 101–118.

Porkka, O. H., 1931. Orientierende Versuche über den täglichen Gang der Bodenatmung. Ann. Soc. Zool.-Bot. Fenn. **15**, 119–132.

Reiners, W. A., 1968. Carbon dioxide evolution from the floor of three Minnesota Forests. Ecology **49** (3), 471–483.

Witkamp, M., 1966. Rates of carbon dioxide evolution from the forest floor. Ecology **47** (3) 492–493.

Witkamp, M., 1969. Cycles of temperature and carbon dioxide evolution from litter and soil. Ecology **50**, 922–924.

Witkamp, M., and M. L. Frank, 1969. Evolution of CO_2 from litter, humus and subsoil of a pine stand. Pedobiologia **9**, 358–366.

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